

## Original Research Article

### Study of estimation of hardness of water using $pH$ –meter

Comment [U1]: The title will be suitable as Study of Water Hardness Estimation using pH-Meter

#### Abstract

Hardness of water is one of the important parameters of water quality. Complexometric titration method is a very common technique to estimate concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  ions individually, which are primarily responsible for water hardness of water. However, the method needs two external indicators to mark the end points of the titrations. Furthermore, accuracy of the method is sacrificed due to inevitable parallax error during marking of end point of titration.

The present work reports that during titration of hard water sample with a complexing agent (~~here,~~  $Na_2EDTA$  solution),  $pH$  changes continuously. This change in  $pH$  is closely monitored and recorded graphically. Hence end point of titration is determined. Additionally, ~~t~~he neutralization volume, thus obtained, is used to estimate  $Ca$  –and  $Mg$  – hardness of the water sample separately. This novel technique obviates the use of any external indicators as well as eliminates any possible parallax error.

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#### Key Words

~~Hardness of water~~ Water hardness, Complexometric titration,  $pH$  –meter etric titration, Buffer solution,  $NaOH$  solution, Disodium EDTA.

#### Introduction

Hardness of water arises primarily due to the presence of profuse amount of  $Ca^{2+}$  and  $Mg^{2+}$  in natural water resources. However, extent of hardness depends on type of land system, e.g., water is soft in hill area, but the same is sufficiently hard in industrial area, commercial area and coastal area. Melian et al.<sup>1</sup> made an attempt to estimate hardness of groundwater and rural drinking water using volumetric titration method. ~~This is a he latter is~~ very popular method of determining water hardness and well documented in the literature<sup>2,4</sup>. Diogo Ferreira et al.<sup>5</sup> reported the uncertainty of visual detection of end point of titration during determination of total hardness of water. Another researcher, ~~P.~~ Sengupta<sup>6</sup> documented the adverse impact of water hardness on health. Ramya et al.<sup>7</sup> studied estimation of hardness in ground water samples using volumetric titration method. Divya et al.<sup>8</sup> reported total hardness and iron content of freshwater resources. Furthermore, the ~~v~~volumetric method of determination of calcium and magnesium hardness of coastal water and sub-surface water is well documented in the literature<sup>9-10</sup>.

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The present work deals with a novel technique, the  $pH$  –metric method, to estimate the concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  ions or in other words, calcium and magnesium hardness of a given water sample.

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## Chemicals and hard water samples

Table 1 Details of chemicals used in this research work

Chemicals	Molecular Weight	Composition
Fused $CaCl_2$	111	Not Applicable (NA)
$MgSO_4 \cdot 7H_2O$	246	NA
$Na_2EDTA$	372	NA
Buffer solution ( $NH_4OH/NH_4Cl$ )	NA	1:1
EBT indicator	461	NA
Murexide indicator	284	NA

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Two different hard water samples are prepared as shown in the Table 2.

Table 2 Composition of hard water samples

Serial No.	Sample Code	$CaCl_2$ (Fused)	$MgSO_4 \cdot 7H_2O$	Weight ratio	Distilled water
1	SC-20	225 mg	0	NA	100 ml
2	SCM-20	150 mg	150 mg	1:1	100 ml

The sample SC-20 is responsible for  $Ca$  –hardness only, while the sample SCM-20 is responsible for both  $Ca$  – and  $Mg$  –hardness.

## Experimental methods

### 1. Volumetric titration

(a) 1 litre standard  $Na_2EDTA$  solution of strength  $0.601 \left(\frac{M}{10}\right)$  is prepared. 40 ml of it is poured into a burette.

(b) 10 ml of hard water sample, SC-20, is taken in a conical flask. 1 ml buffer solution along with a pinch of EBT indicator is added into the conical flask. The solution turns to wine red colour. It is then titrated against  $Na_2EDTA$  solution, running from the burette. At the end point wine red colour changes to sky blue. Initial and final readings are noted. Three such readings are recorded. Total hardness can be calculated using the mean burette reading.

(c) For the hard water sample, SCM-20, the process (b) is followed. Here also three readings are recorded. Total hardness, i.e., hardness due to  $Ca^{2+}$  and  $Mg^{2+}$  can be calculated using the mean burette reading.

(d) 10 ml of hard water sample, SCM-20, is taken in a conical flask. Add 1 ml 1(N)  $NaOH$  solution. The function of  $NaOH$  is to block  $Mg^{2+}$  to avoid formation of any  $Mg$  –complex during titration process. Add a pinch of Murexide indicator. The solution turns to pink colour due to formation of [ $Ca$  – Murexide]. It is then titrated against  $Na_2EDTA$  solution, running from the burette, till the pink colour changes to purple. Initial and final readings are noted. Three such readings are recorded.  $Ca$  –hardness can be calculated using the mean burette reading.

(e) Using the results of the processes (c) and (d)  $Mg$  –hardness can be calculated by subtracting  $Ca$  –hardness from the total hardness.

## 2. pH –metric titration

(a) 20 ml of prepared  $Na_2EDTA$  solution is poured into another burette.

(b) 10 ml hard water sample, SC-20, is taken in a 250 ml beaker. 90 ml distilled water is added into it in order to immerse the electrodes safely into the solution. 1 ml buffer solution is added into the beaker. Shake the mixture and immerse the pH electrode-set into it. Take the 1<sup>st</sup> reading. The beaker is taken out and 0.5 ml  $Na_2EDTA$  solution is added into it from the burette. Shake the mixture and pH electrode-set is again immersed into it. Take the 2<sup>nd</sup> reading. The process is continued till the pH reads around 10.

(c) The pH readings are plotted against volume of  $Na_2EDTA$  solution added.

(d) The step (b) is repeated for the other hard water sample, SCM-20. In this case also, pH readings are plotted against volume of  $Na_2EDTA$  solution.

(e) In case of SCM-20 hard water sample, the step (b) is repeated once more using 1 ml 1(N) NaOH solution instead of 1 ml buffer solution. The pH readings are plotted against volume of  $Na_2EDTA$  solution added.

## Results and Discussion

### 1. Sample SC-20

This sample contains only  $Ca^{2+}$  ions. The results of volumetric titration of the sample are shown in the Table 3.

**Table 3 Volumetric titration for the hard water sample SC-20**

No. of observations	Volume of SC-20 sample hard water taken (ml)	Volume of $Na_2EDTA$ consumed (ml)			
		Initial	Final	Difference	Mean volume
1	10	0	1.8	1.8	1.8
2	10	1.8	3.7	1.9	
3	10	3.7	5.5	1.8	

The mean volume (1.8 ml) represents the volume of  $Na_2EDTA$  required to absorb all  $Ca^{2+}$  ions from the aliquotted sample solution (10 ml) to form stable  $[Ca - EDTA]$  complex.

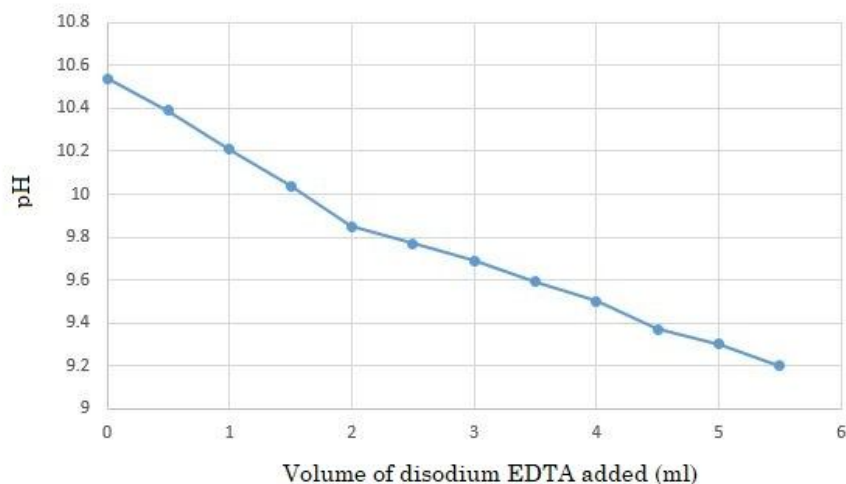
The results of pH –metric titration of the sample SC-20 are shown in the Table 4.

**Table 4 pH-metric titration for the hard water sample SC-20**

No. of observations	Volume of $Na_2EDTA$ solution added (ml)	Total volume of $Na_2EDTA$ solution added (ml)	pH reading
1	0	0	10.54

2	0.5	0.5	10.39
3	0.5	1	10.21
4	0.5	1.5	10.04
5	0.5	2	9.88
6	0.5	2.5	9.77
7	0.5	3	9.69
8	0.5	3.5	9.59
9	0.5	4	9.5
10	0.5	4.5	9.37
11	0.5	5	9.3
12	0.5	5.5	9.2

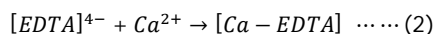
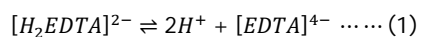
pH –readings are plotted against volume of  $Na_2EDTA$  solution added. It is shown in the Fig.1.



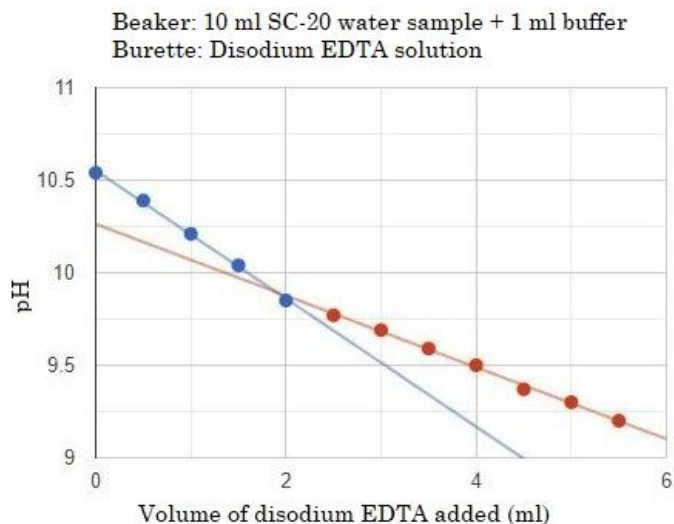
**Figure 1 SC-20 sample: plot of pH –readings versus volume of titrant added.**

Two straight lines with different slopes are quite distinguished from the Fig.1. These two straight lines are drawn separately in the Fig.2.

EDTA has four acidic H-atoms. So, it is best represented by  $H_4EDTA$ . In aqueous solution disodium salt of EDTA or  $Na_2H_2EDTA$  dissociates to form  $[H_2EDTA]^{2-}$ . The latter reversibly dissociates to produce  $[EDTA]^{4-}$ , which forms complexes with metal cations. In case of SC-20 hard water sample, only one type of complex, i.e.,  $[Ca - EDTA]$  is formed. The reactions are given below



The buffer consumes the  $H^+$  ions, accelerating formation of  $[EDTA]^{4-}$  so that the latter is able to form stable complex,  $[Ca - EDTA]$ . As the reaction continues, concentration of  $[OH]^-$  in buffer decreases, due to which, sharp drop of  $pH$  is observed (blue curve in the Fig.2) till the end point is reached. After the end point the 2<sup>nd</sup> step of the above reaction [Equation (2)] ceases to occur and hence only a slow change in  $pH$  is observed due to buffer action (red curve in the Fig.2).



**Figure 2 SC-20 sample: Linear plot of  $pH$  –readings versus volume of titrant added.**

Intersection of the two straight lines occurs at 1.9 ml, which is assumed to be the end point of titration. So, the end point, obtained by  $pH$  –metric method, is almost same as that obtained by volumetric method (Table 2).

## 2. Sample SCM-20

This sample contains both  $Ca^{2+}$  and  $Mg^{2+}$  ions. Two sets of volumetric titrations are performed to estimate the individual concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  ions. Two sets of  $pH$  –metric titrations are also performed.

### Set-1

#### 1. Volumetric titration using 1 ml buffer solution.

**Table 5-5 Volumetric titration for the hard water sample SCM-20**

No. of observations	Volume of SCM-20 sample hard water taken (ml)	Volume of $Na_2EDTA$ consumed (ml)			
		Initial	Final	Difference	Mean volume
1	10	0	2.5	2.5	2.4
2	10	2.5	4.8	2.3	

3	10	4.8	7.2	2.4	
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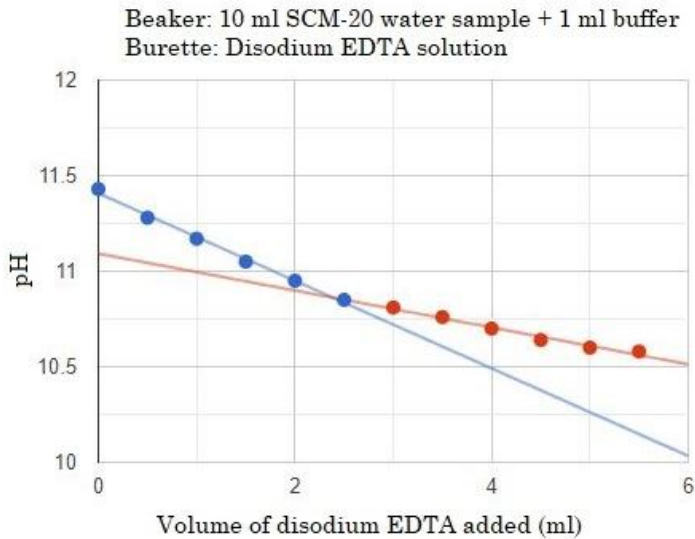
The mean volume (2.4 ml) represents the volume of  $Na_2EDTA$  required to absorb all  $Ca^{2+}$  and  $Mg^{2+}$  ions from the aliquotted sample solution (10 ml) to form stable  $[Ca - EDTA]$  and  $[Mg - EDTA]$  complexes.

## 2. pH –metric titration using 1 ml buffer solution.

**Table 6** pH-metric titration for the hard water sample SCM-20

No. of observations	Volume of $Na_2EDTA$ solution added (ml)	Total volume of $Na_2EDTA$ solution added (ml)	pH reading
1	0	0	11.43
2	0.5	0.5	11.28
3	0.5	1	11.17
4	0.5	1.5	11.05
5	0.5	2	10.95
6	0.5	2.5	10.85
7	0.5	3	10.81
8	0.5	3.5	10.76
9	0.5	4	10.7
10	0.5	4.5	10.64
11	0.5	5	10.6
12	0.5	5.5	10.58

The plot of pH –readings versus volume of disodium EDTA gives rise to two straight lines of different slopes as shown in the Fig.3.



**Figure 3** SCM-20 sample in presence of buffer: Linear plot of pH-readings versus volume of titrant added.

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Intersection of the two straight lines occurs at 2.52 ml, which is believed to be the end point of titration. So total hardness due to  $Ca^{2+}$  and  $Mg^{2+}$  ions can be calculated *pH* –metrically.

#### Set-2

1. Volumetric titration is performed using 1 ml 1(N)NaOH solution.

**Table 7** Volumetric titration for the hard water sample SCM-20

No. of observations	Volume of SCM-20 sample hard water taken (ml)	Volume of $Na_2EDTA$ consumed (ml)			
		Initial	Final	Difference	Mean volume
1	10	0	1.6	1.6	1.6
2	10	1.6	3.2	1.6	
3	10	3.2	4.9	1.7	

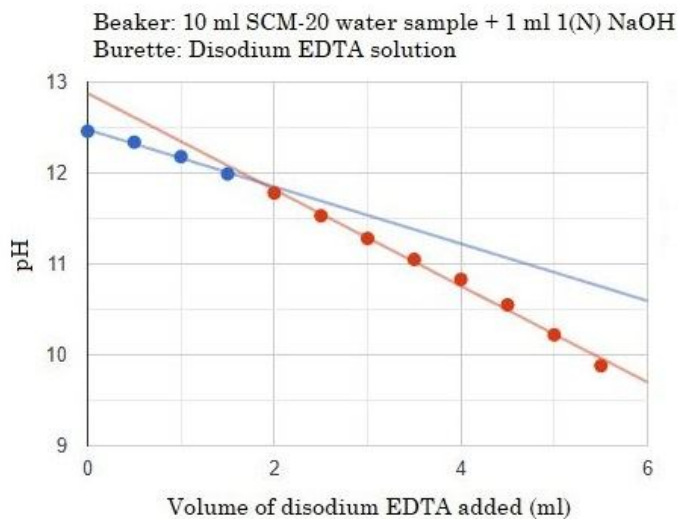
The mean volume (1.6 ml) represents the volume of  $Na_2EDTA$  required to absorb all  $Ca^{2+}$  from the aliquotted sample solution (10 ml) to form stable  $[Ca - EDTA]$  complexes.

2. *pH* –metric titration using 1 ml 1(N)NaOH solution.

**Table 8 pH-metric titration for the hard water sample SCM-20**

No. of observations	Volume of $Na_2EDTA$ solution added (ml)	Total volume of $Na_2EDTA$ solution added (ml)	$pH$ reading
1	0	0	12.46
2	0.5	0.5	12.34
3	0.5	1	12.18
4	0.5	1.5	11.99
5	0.5	2	11.78
6	0.5	2.5	11.53
7	0.5	3	11.28
8	0.5	3.5	11.05
9	0.5	4	10.83
10	0.5	4.5	10.55
11	0.5	5	10.22
12	0.5	5.5	9.88

The similar plot of  $pH$  –readings versus volume of disodium EDTA is shown in the Fig.4.



**Figure 4 SCM-20 sample in presence of NaOH: Linear plot of pH-readings versus volume of titrant added.**

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Intersection of the two straight lines occurs at 1.74 ml, which is believed to be the end point of titration. So hardness, due to  $Ca^{2+}$  ions only, can also be calculated  $pH$  –metrically. Using the results of Fig.3 and Fig.4, hardness due to  $Mg^{2+}$  ions can be calculated.

According to Table 1, in the hard water sample SCM-20 ratio of weights of  $CaCl_2$  and  $MgSO_4 \cdot 7H_2O$  is 1:1. So the following relation holds good

$$\frac{Ca - hardness}{Mg - hardness} = \frac{MW \text{ of } MgSO_4 \cdot 7H_2O}{MW \text{ of } CaCl_2} = \frac{246}{111} = 2.216$$

If  $V_{Ca}$  and  $V_{Mg}$  are the volumes (in ml) of  $Na_2EDTA$  consumed due to  $Ca^{2+}$  ions and  $Mg^{2+}$  ions respectively, the following relation also holds good.

$$\frac{Ca - hardness}{Mg - hardness} = \frac{V_{Ca}}{V_{Mg}}. \text{ So, } \frac{V_{Ca}}{V_{Mg}} = 2.216 \text{ (Using theoretical approach)}$$

(a) Considering volumetric titration results of sets 1 and 2 (Table 4 and Table 6), the following equations are true

$$V_{Ca} + V_{Mg} = 2.4 \text{ ml and } V_{Ca} = 1.6 \text{ ml. So, } V_{Mg} = 0.8 \text{ ml}$$

$$\text{So, } \frac{V_{Ca}}{V_{Mg}} = 2 \text{ (Using volumetric titration approach)}$$

(b) Considering  $pH$ -metric titration results of sets 1 and 2 (Fig.3 and Fig.4), the above equations become

$$V_{Ca} + V_{Mg} = 2.52 \text{ ml and } V_{Ca} = 1.74 \text{ ml. So, } V_{Mg} = 0.78 \text{ ml}$$

$$\text{So, } \frac{V_{Ca}}{V_{Mg}} = 2.23 \text{ (Using } pH \text{-metric titration approach)}$$

So,  $pH$ -metric titration result is very close to the theoretical value compared to the volumetric titration result. Thus, it is believed that  $pH$ -metric titration method is more accurate than volumetric titration method.

## Conclusions

1. Hardness of a given water sample can be estimated accurately using  $pH$ -meter.
2. The  $pH$ -metric determination of water hardness of water is more accurate than volumetric determination. Additionally, of the same as the end point of titration in the  $pH$ -metric method is obtained from the graph without any parallax error.
3. No indicator is required in  $pH$ -metric method of determination of hardness of water, which is considered a distinct advantage over volumetric method.
4. This novel technique of determination of hardness of water is expected to explore future research works, based on  $pH$ -meter.

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